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GB 1463387

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(54) **Monitoring hydrocarbons in
air**

(57) In a process for monitoring total hydrocarbons and also the concentrations of the individual hydrocarbon components in a gas or vapour mixture, for example in air, total hydrocarbon concentration is measured by a flame-ionisation detector, a portion of the mixture is passed through a chromatographic column, which separates the components from each other and the separated components are fed in succession to a flame-ionisation detector, which measures their respective concentrations. The apparatus thus measures continuously both total hydrocarbon concentration and the concentrations of the individual components. If total hydrocarbon concentration, or if the concentration of any component, exceeds the

specified safe value, the plant is automatically shut down.

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SPECIFICATION

Process and apparatus for continuously monitoring a gas mixture

5 The invention relates to a process for continuously monitoring the composition of a gas or vapour mixture, particularly for continuously measuring both total hydrocarbons and also
10 the individual hydrocarbons components in a mixture of hydrocarbons in air by means of flame ionisation.

Flame ionisation itself and the use of flame-ionisation detectors for measuring, for
15 example, hydrocarbon concentrations in air are known in the prior art.

A flame-ionisation detector has a flame burning a fuel gas either in air or in oxygen. A stream of the gas mixture under investigation
20 is fed into the detector, which has a pair of electrodes at different electric potentials, i.e. a d.c. voltage is applied across them. An electric current flows between the electrodes, the value of the current being proportional to the
25 concentration of hydrocarbons in the gas mixture.

A flame-ionisation detector of this kind can be used, for example, for measuring the total hydrocarbon concentration in the exhaust
30 gases of an automobile. But a flame-ionisation detector alone is not sufficient for monitoring the atmosphere in a paint-spray chamber in a motor-car factory, which contains several individual gas or vapour components.

35 The atmosphere in a paint-spray chamber usually contains a variety of different hydrocarbon components, including some which are toxic when breathed. Other hydrocarbon components are explosive with their concentrations
40 exceed a certain safety limit and consequently it is necessary to ensure that this limit is not exceeded. Other components of the spray-chamber atmosphere, on the other hand, are neither explosive nor a danger to
45 health.

In attempting to monitor these atmospheres it is conventional to use flame-ionisation detectors, of which there can, for example, be one for each spray chamber. Each flame-ionisation detector measures total hydrocarbon
50 concentration in the gas mixture, and when this exceeds a certain critical value the installation is automatically shut down.

But in practice a measurement of total hydrocarbon concentration is not sufficient to ensure safety because different components of the gas mixture have different safe concentrations. For example, it can happen that while one component of the mixture increases in its
60 concentration, another component decreases, no detected change occurring in total hydrocarbon concentration although, in fact, the component which is increasing is approaching its own safe concentration limit, producing a
65 dangerous situation in regard to explosion or

toxic vapour hazard.

The intention in the present invention is therefore to provide a process for continuously monitoring gas mixtures in such a way that
70 there are measured not only total hydrocarbon concentration but also the concentration or at least one of the individual components of the mixture.

The problem is solved, according to the
75 invention, in that a first portion of the mixture is fed to a flame-ionisation detector which measures total hydrocarbon concentration in the mixture, a second portion being passed through a chromatographic column which separates the individual components from each
80 other, these being then fed in succession to a flame-ionisation detector, which successively measures their individual concentrations in the mixture.

85 The signals delivered by the flame-ionisation detector for the individual components of the mixture are applied to a computer for storage in its memory, the contents of the memory being repeatedly updated, i.e. deleted and re-constructed.

Each flame-ionisation detector is calibrated using a calibration gas, such as CH_4 , and the signal delivered by the detector is proportional to the number of carbon atoms in the sample
95 of the gas. To determine the concentration in the gas mixture of any other hydrocarbon component, the computer must therefore multiply the value of the signal delivered by the detector by the ratio of the number of carbon atoms in a molecule of calibration gas, to the
100 number of carbon atoms in a molecule of the component gas.

The computer can deliver its output signals to indicators for displaying the latest results of
105 the measurements on the components of the gas mixture, the results being repeatedly updated. Alternatively, if desired, the computer can apply its output signals to the flame-ionisation detector which follows the chromatographic column or to the indicator connected to this detector, so that the indicator displays, one after the other, the concentrations of the individual components of the
110 mixture.

115 With advantage, a further portion of the gas mixture is passed through at least one further chromatographic column, followed by at least one further flame-ionisation detector, the several chromatographic columns operating in alternation, time-shifted relative to each other, in order to shorten the interval between measurements.

Several examples of the invention will now be described with the help of the sole figure
125 of the drawing, which illustrates an apparatus for performing the process of the invention.

The apparatus comprises two flame-ionisation detectors 12 and 14, each having, as is conventional, a burner and electrodes the resulting electric signals being amplified in am-
130

plifiers 38 and 42. Each flame-ionisation detector 12, 14 is fed with a fuel gas (for example H_2) and an oxidising gas such as O_2 or synthetic air.

- 5 The amplifiers 38, 42 apply electric signals to indicators 40, 44.

The gas mixture under investigation is fed through a feed-passage 20 and through separate passages 22 and 24 to the flame-ionisation detectors 12 and 14.

- 10 The gas mixture arriving through the feed-passage 20 can contain several gas or vapour components deriving, for example, from a paint-spray booth in a motor-car factory, including evaporated solvents.

The portion of the gas mixture flowing through the passage 24 is analysed in the detector 14, in the known manner, to determine total hydrocarbon content, the measured value being applied in the form of an electric signal, over the amplifier 42, to the indicator 44 which can, if desired, be connected to a safety device (not shown). When the signal reaching the indicator 44 exceeds a safe value, the safety device responds by emitting an audible alarm, or by switching the installation off.

- 25 The detector 14 therefore delivers a continuous indication of the total hydrocarbon content in the gas mixture under investigation.

The value of the signal delivered by the detector 14 is proportional to the total number of carbon atoms in the sample of gas mixture, which comprises several components. Consequently, when the concentration in the gas mixture of a higher hydrocarbon (containing more carbon atoms in the molecule) increases, the value of the delivered electric signal rises more than it would do if the concentration of a lower hydrocarbon were increasing in like manner. In other words, the indication does not convey which components of the gas mixture are increasing in concentration, nor by how much each one is increasing.

- 30 In particular, the information on total hydrocarbon content does not convey whether a particular component of the gas mixture is approaching a dangerously high concentration, or not.

35 In order to obtain information on the concentrations of the individual hydrocarbon components in the gas mixture under investigation, the mixture is passed through a chromatographic column 36. The gas mixture arriving through the feed passage 20 is fed through the passage 22 to a metering valve 16 which works, in conjunction with a metering loop 18, to deliver metered portions of gas to the chromatographic column 36 which is, in turn, followed downstream by the flame-ionisation detector 12.

- 40 The metering valve 16, with its metering loop 18, are of known construction and need not be described in detail here. What these two devices do is feed a succession of equal

metered doses of the gas mixture, one after the other to the chromatographic column 36.

The chromatographic column 36 takes about one minute to analyse each metered dose of the gas mixture. During each analysis supply of gas through the passage 22 is interrupted by the valve 16, the unwanted stream of gas flowing, for example, out to the ambient atmosphere. As soon as the analysis in the chromatographic column 36 has been completed, the metering valve 16 switches over, sending the dose of gas in the metering loop 18 to the chromatographic column 36, where it is analysed in turn, and so on.

- 70 The column 36 separates the individual components of the gas mixture from each other, delivering them in succession to the detector 12, which measures the hydrocarbon concentration of each component and delivers a corresponding signal over amplifier 38 to the indicating instrument 40.

In many cases it is sufficient to use a simpler modification of the apparatus 10. In this case the detector 12, the amplifier 38 and the indicator 40 are omitted. From the column 36 the individual components of the gas mixture are conveyed through a passage 52 and through a selector valve 56 to the other detector 14, which measures hydrocarbon concentration in the component. The sequence of measurements made by the detector 14 is therefore as follows: First the gas mixture arriving through the passage 24 and through the selector valve 54 is measured for its total hydrocarbon concentration. Then, after column 36 had completed its separation, selector valve 54 is switched over, obturating passage 24, the separated components arriving one after the other from column 36, through passage 52 and valve 54, are analysed successively by the flame-ionisation detector 14.

- 80 Nevertheless, in most practical applications a separate detector 14 is used for total hydrocarbons and at least one detector 12 for the analysis of the individual components.

In further development of the invention, a computer 30 is provided, for adding up the signals from detector 12. An electric conductor 26 applies the signals from detector 12 to the computer 30, which has a group of memory devices. The readings of the memory devices are up-dated, i.e. deleted and re-constructed, every time the column 36 has completed a fresh separation, whereupon the detector 12 sends fresh signals in succession, one for each component of the gas mixture, to the memory devices, which have been cleared ready for receiving the new information. Each memory device therefore always contains up-to-date information on the hydrocarbon concentration in the particular component of the mixture.

- 125 As already mentioned, each flame-ionisation detector 12, 14 delivers a signal whose value

is proportional to the number of carbon atoms detected. The apparatus is calibrated with the help of a calibration gas. For example the ionisation detector 12 is adjusted so that when air containing 30 ppm (parts per thousand) of calibration gas is analysed, this gives an indication of 30 graduations on the indicator scale. But when a different gas is analysed, a scale reading of 30 graduations does not, of course, still indicate that there are 30 ppm of the new hydrocarbon gas in the air, or in the gas mixture. What it indicates is merely that the number of carbon atoms is the same as before.

This point will now be elucidated in greater detail with the help of an example.

Let it be assumed that the apparatus has been calibrated using CH_4 , so that 30 ppm of CH_4 in the calibration gas mixture produce a deflection of 30 scale graduations on the indicators 40 and 44.

The gas mixture being investigated is then fed continuously to the apparatus. A portion of the gas mixture therefore flows continuously to the flame-ionisation detector 14. The remainder of the stream of gas mixture is applied to the chromatographic column 36 for analysing by the flame-ionisation detector 12. And let it be assumed that the indicator 44

shows a deflection of 90 scale graduations. This amount of deflection could represent 90 ppm of CH_4 in the gas mixture, if the hydrocarbon being measured were CH_4 . But if the hydrocarbon were C_2H_6 the indicator deflection of 90 scale graduations would represent only 45 ppm of this hydrocarbon. And for C_3H_8 the same indicator deflection would represent only 30 ppm of the hydrocarbon. If two or more of these hydrocarbons were present in the gas mixture the deflection of 90 on the scale of indicator 44 would not allow any quantitative conclusion to be drawn on the ppm of hydrocarbons in the gas mixture. In all cases the answer is provided by the chromatographic column 36, which separates the components of the gas mixture and then feeds them in succession to the flame-ionisation detector 12, successive scale deflections consequently appearing on the indicator 40.

To illustrate the process used, let it be assumed that in a first step the chromatographic column 36 feeds CH_4 to the detector 12, the indicator 40 showing a deflection of 30 graduations, indicating 30 ppm of CH_4 in the gas mixture reaching the apparatus. And let it be assumed, further, that in a second step the chromatographic column 36 feeds C_2H_6 to the detector 12, again producing 30 graduations of deflection on the indicator 40, representing the fact that there are 15 ppm of C_2H_6 in the gas mixture (30 divided by 2). In a third step (let it be assumed) the chromatographic column 36 feeds C_3H_8 to the flame-ionisation detector 12, again producing (let us assume) a deflection of 30 graduations on the indicator

40. Dividing 30 by 3, we find that this represents 10 ppm of C_3H_8 . The result of the analysis therefore gives 30 ppm of CH_4 , together with 15 ppm of C_2H_6 and 10 ppm of C_3H_8 in the gas mixture being analysed by the apparatus.

As already mentioned, the electric signals delivered by the flame-ionisation detector 12 are processed by the computer 30, which divides the signals for C_2H_6 by 2, and those for C_3H_8 by 3. The processed signals can, if desired be delivered by 30 to three final indicators 32, 33, 35 which display digital or analog values for each of the three gas-mixture components CH_4 , C_2H_6 and C_3H_8 . The displays are up-dated, i.e. deleted and re-constructed, each time a sample-dose of the gas mixture is processed by the chromatographic column 36.

In consequence, the three final indicators 32, 33, 35 constantly display, in this example of the process, the ppm of each of the three components CH_4 , C_2H_6 and C_3H_8 in the gas mixture, the values shown being up-dated intermittently at the intervals of time taken by chromatographic column 36 to process each sample-dose of gas mixture.

Connected to the computer 30 is a safety detector 34, which emits an audible alarm and/or shuts the plant down, whenever the ppm of any one of the components of the gas mixture exceeds its safety limit.

Assuming, for example, that the interval of time required for each analysis is 1 minute, then a fresh display for each component appears on the final indicators 33, 34, 35 each minute. However, this interval of time can be shortened, according to the invention, by providing at least one further chromatographic column 58 in parallel to the column 36, the two columns being timed to alternate so that analysis takes place at twice the frequency. The extra column 58 feeds samples to a further flame-ionisation detector 60 which sends its signal over an amplifier 62 to an indicator 64.

In this case a selector valve 56 is provided between the metering valve 16 and the chromatographic column 36, the selector valve 56 switching over every 30 seconds, so that first a sample-dose of gas mixture is supplied to column 36 and then, 30 seconds later, a dose to column 58, each chromatographic column taking, in this example, one minute to process its sample-dose.

The computer 30 therefore receives the signals from detector 60 each time 30 seconds after receiving the signals from detector 12.

The signals from detector 60, amplified by the amplifier 62, are transmitted over a conductor 66 to the computer 30, which processes them in the same way as it processes the signals arriving over the conductor 26, with the consequence that now the final indi-

cators 32, 33, 35 are up-dated every 30 seconds.

It will be observed that by using three chromatographic columns in parallel, up-dating of the displayed values can occur every 20 seconds and further chromatographic columns can make this interval shorter, so that ultimately a nearly continuous display can be obtained for each component of the gas mixture.

As an alternative to the indicators 32, 33, 35, or in addition to them, the computer 30 can, if desired, transmit over a conductor 46, processed signals to the indicator 40, so that this indicator displays, for each component, a read-out signal directly showing the concentration, in ppm, of this component in the gas mixture. And, if desired, the computer 30 can do the same thing, over a conductor 68, for the indicator 64.

Referring back to the simple version of the invention previously described, which has only one flame-ionisation detector, the one shown at 14 in the figure, the signals from this, after amplification in 42, can be transmitted over a conductor 48 to the computer 30 and then, after processing in the computer, transmitted over a conductor 50 to the indicator 44, so that this indicator first displays total hydrocarbon content and then, one after the other, the concentrations of the individual components.

In a further example of the invention, not shown in the drawing, there can be provided, in addition to the detector 14, which measures total hydrocarbon concentration, one further detector for each component of the mixture. Each further detector receives the same gas mixture as does detector 14, and each is connected to the computer 30. Let it be assumed that the first further detector measures CH_4 , the second C_2H_6 and the third C_3H_8 . From the signal delivered by the detector for CH_4 there are deducted, before the signal reaches the indicator, the values calculated by the computer for C_2H_6 and C_3H_8 , so that the signal reaching the indicator represents the concentration of CH_4 in the mixture. From the signal delivered by the detector for C_2H_6 there are deducted the values calculated for CH_4 and C_3H_8 , giving a signal representing C_2H_6 . From the signal delivered by the detector for C_3H_8 there are deducted the values calculated for CH_4 and C_2H_6 , giving a signal representing C_3H_8 .

The three signals delivered by the three detectors therefore represent the concentrations of the three components CH_4 , C_2H_6 and C_3H_8 in the mixture, and these signals are repeatedly up-dated, the frequency of the up-dating being determined by the time taken for the chromatographic column to process the sample.

Instead of using three detectors one can, if desired, use only one, provided that this de-

tector is switched over repeatedly to measure first CH_4 , then C_2H_6 , then C_3H_8 , then CH_4 again and so on, constantly repeating this cycle.

It has been found in practical tests that a satisfactory monitoring, for example of a paint-spray booth, is usually obtained using only two chromatographic columns operating in parallel and providing a fresh set of displays every 30 seconds. Nevertheless in certain cases it can be desirable to use more chromatographic columns so as to obtain fresh displays every 20 seconds, or even at 10 second intervals.

Should it happen that during this short time interval (of 30, or 20 or 10 seconds) an excessive total hydrocarbon concentration occurs, then this can serve as a preliminary indication of trouble. The flame-ionisation detector 14 indicates the excessive total hydrocarbon concentration. Apart from any automatic shutting down of the installation, it can be arranged that as soon as excessive total hydrocarbon concentration occurs, as indicated by detector 14, a sample of the gas mixture is stored in a second metering loop 28 of the metering valve 16. Subsequently, as soon as the chromatographic column 36 (or 58) is free, the sample is fed to this, or it can be fed to a separate chromatographic column, for separation and analysis of the individual components.

This analysis reveals which of the components caused the excessive total hydrocarbon concentration, i.e. it reveals what the gas composition was at the time.

As described further above, the apparatus can have indicators 32, 33, 35 as alternatives to, or in addition to, the indicators 44 and 64. But if desired the apparatus can be operated perfectly well without these extra indicators, using only the indicator 44 for giving the desired information. In this case the detector 12 transmits its signals, as described before, to the computer 30, which processes them to give the concentrations of (in this example) CH_4 , C_2H_6 and C_3H_8 . This information is fed, over a separate conductor which is not shown in the figure, to the indicator 44.

It will be recalled that indicator 44 at this time indicates total hydrocarbon concentration in the gas mixture so that, in this example, the indicator 44 shows a deflection of 90 scale graduations. At this point in time the computer 30 sends to indicator 44 a signal which deducts the values for C_2H_6 and C_3H_8 from the total hydrocarbon concentrations, so that indicators 44 now shows, in ppm, only the concentration of CH_4 in the mixture. The process is repeated, the computer 30 this time deducting the values for CH_4 and C_3H_8 from the total hydrocarbon concentration, so that indicator 44 now discloses the concentration of C_2H_6 . Finally, the values for CH_4 and C_2H_6 are deducted, the indicator 44 now

indicating the concentration of C_3H_8 , in ppm. The selections in the computer 30 can be effected with the help of conventional circuit devices.

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CLAIMS

1. A process for continuously monitoring the composition of a gas or vapour mixture, such as for continuously measuring both total hydrocarbons and also the individual hydrocarbon components in a mixture of hydrocarbons in air, by means of flame ionisation, characterised in that a first portion of the mixture is fed to a flame-ionisation detector which measures total hydrocarbon concentration in the mixture, a second portion being passed through a chromatographic column which separates the individual components from each other, these being then fed in succession to the same or another flame-ionisation detector or detectors to measure the individual concentrations in the mixture.

2. A process according to claim 1 characterised in that the individual components are fed to a single flame-ionisation detector which successively measures their individual concentrations in the mixture.

3. A process according to claim 2 characterised in that the single detector is the same as the one used for the first portion of the mixture.

4. A process according to claim 1, 2 or 3 characterised in that the electrical signals delivered by the flame-ionisation detector or detectors following the chromatographic column are applied to a computer which stores the signals in a memory and transmits them to an indicator which displays them, the contents of the memory being repeatedly up-dated.

5. A process according to claim 4 wherein a number of flame ionisation-detectors are all calibrated using the same calibration gas, characterised in that the values of the electrical signals delivered by the flame-ionisation detector or detectors following the chromatographic column are multiplied in the computer by the ratio of the number of carbon atoms in the molecule of the calibration gas to the number of carbon atoms in the molecule of the component gas.

6. A process according to claim 5 characterised in that the signal delivered by the flame-ionisation detector for total hydrocarbons is applied to the computer which corrects the signals for the individual components, so that the computer delivers not only a signal for total hydrocarbons but also corrected signals for the individual components of the mixture.

7. A process according to claim 5 characterised in that each individual component has its own flame-ionisation detector whose delivered signal is corrected by the computer so that each flame-ionisation detector delivers information on only one of the components.

8. A process according to one of the preceding claims characterised in that a further portion of the mixture is fed to a further chromatographic column and from there to a flame-ionisation detector, the chromatographic columns being operated in alternation, time displaced relative to each other, so that the apparatus delivers analysis results at shorter intervals.

9. A process according to one of the preceding claims characterised in that when the flame-ionisation detector for total hydrocarbons detects an excessive value, a portion of the mixture is stored and passed through a chromatographic column followed by a flame-ionisation detector, so that information is obtained on which of the individual components has caused the excessive total hydrocarbon concentration in the mixture.

10. Apparatus for continuously monitoring the composition of a gas or vapour mixture, such as for continuously measuring both total hydrocarbons and also the individual hydrocarbon components in a mixture of hydrocarbons in air, by means of flame-ionisation, comprising a flame-ionisation detector arranged to measure total hydrocarbon concentration in a first portion of the mixture, a chromatographic column arranged to receive a second portion of the mixture so as to separate the individual components from each other, and means for feeding these components to the same or another flame-ionisation detector or detectors so as to measure their individual concentrations in the mixture.

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